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EXAFS Study of Cu(II) Adsorption Complexes at the Calcite Surface

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Beamline(s): X18B

Introduction: Previous studies have shown that calcium carbonates have a high affinity for Cu(II), and that sorption proceeds rapidly, which implies that these minerals may be an important sink for Cu retention in natural systems [1,2]. In this study, we performed EXAFS analyses of Cu(II)-calcite adsorption samples to characterize the interaction between Cu(II) and the calcite surface at the molecular scale.

Methods and Materials: The calcite sorbent used in this study had an N_2-BET surface area of 10 $m^2\ g^{-1}$. Before reaction with Cu(II), calcite-water suspensions of 0.1 or 0.5 g calcite L^{-1} were equilibrated at atmospheric CO_2 pressure for 2 months, yielding an equilibrium pH of 8.3. The suspensions were then spiked with appropriate aliquots of a 0.01M $CuCl_2$ stock solution to achieve initial Cu concentrations of 1 or 5 μM. Following reaction for 48h, the suspensions were filtered through 0.22 μm filter paper to collect the wet calcite solids for EXAFS characterization. Room temperature scans were taken at the Cu K-edge, using a 13-element solid state detector for fluorescence detection. A number of reference Cu solid standards were also run for comparison with the Cu-calcite adsorption samples. Data analysis was done with WinXAS2.0 [3], in combination with the FEFF7 code [4], following standard procedures.

Results: Figure 1 shows the k^3-weighted χ spectra of the Cu(II)-calcite adsorption samples, along with those of the Cu reference compounds. None of the reference spectra matches those of the sorption samples, indicating that precipitation of these phases had not occurred to any noticeable extent in the sorption experiments. The adsorption spectra are also different from the spectrum of a dilute Cu-calcite solid solution, which indicates that during the reaction time allowed, no significant incorporation of Cu into the calcite structure had occurred. The Fourier transforms of the k^3-weighted χ spectra are shown in Figure 2. Fitting results indicated that the first-neighbor O shell of the Cu adsorption complexes are located at a radial distance of ~1.95 Å. This is the equatorial O shell of the Jahn-Teller distorted Cu complexes at the calcite surface. No contribution of the axial O shell could be identified, which indicates a high degree of disorder in the Cu-O_{axial} correlation. Peaks present in the RSFs located beyond the first O shell were successfully fit with O, C and Ca shells located at radial distances consistent with Cu positioned in unoccupied Ca sites at the calcite surface, most likely at kinks and step sites, which contain CO_3 ligands that are only partially coordinated by lattice atoms. We therefore conclude that Cu(II) forms Jahn-Teller distorted inner-sphere complexes at the calcite surface by direct coordination to surface CO_3 groups.

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References:

[1] Compton R.G., and Pritchard K.L. (1990) J. Chem. Soc. Faraday Trans. 86, 129-136.
[2] Franklin M.L. and Morse J.W. (1982) Ocean Sci. Engn. 7, 147-174.
[3] Ressler T. (1997) J. Physique IV, 7, C2-269.
[4] Zabinskly S.I., Rehr J.J., Ankudinov A., Albers R.C., and Eller M.J. (1995) Phys. Rev. B52, 2995-3009.

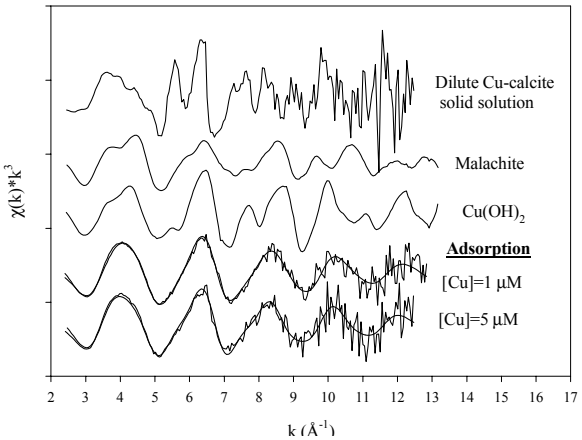

Figure 1. χ structures of the various samples

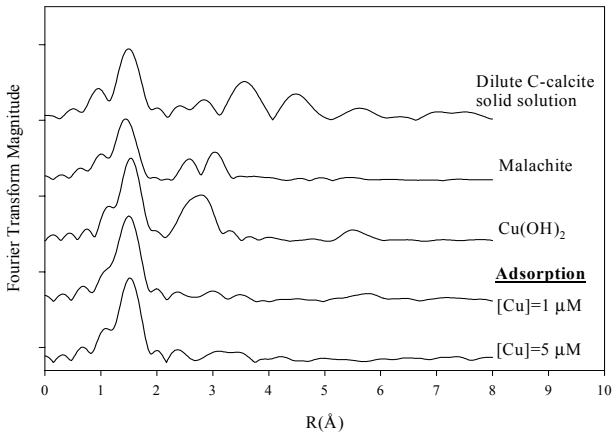

Figure 2. RSFs of the samples analyzed